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Preparation and Performance Characterization of Copper and Diamond Filled Composite Thermal Conductivity Materials

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Abstract

An experimental investigation was conducted to prepare and study the thermal conductivity performance of copper and diamond composite materials. Copper powder and diamond particles were used as fillers, epoxy resin was used as matrix, and composite materials were prepared by vacuum-assisted mechanical stirring. The thermal expansion coefficient of different composite materials was measured by a laser flash method, which can be used to calculate the thermal conductivity. The effect of the filling rate of copper powder, the morphology of copper powder, the filling rate of diamond, and the thermal conductivity of the particles on the thermal conductivity of composite materials was studied. The results showed that thermal conductivity of copper powder and diamond particles composite materials were 874% and 535% higher than that of the epoxy resin when their filling rates were 50.3 vol.% and 40.0 vol.%, respectively. For two-dimensional flake copper powder materials, the thermal conductivity could be effectively improved at a lower filling rate. However, the flake particles were easy to aggregate at a high filling rate, which maybe cause the composite materials to pulverize.

Keywords Thermal interface material · Thermal conductivity · Copper powder · Diamond particles · Filling rate

Introduction

With the development of semi-conductor technology and integration in the field of microelectronics, wide band-gap materials are more suitable for application in high-power, high-performance and high-density integrated electronic devices and equipment (Huang et al. 2011; Prasher 2006;

Due and Robinson 2013), such as aerospace, automobiles equipment, high-power LEDs, high-performance data centers, smartphones and medical equipment, etc. However, the high-density integrated packaging will cause the heat flux inside the power device to increase significantly and the local heat generated during operation will increase rapidly, seriously affecting the performance of the device. Studies has shown that about 55% of high-power devices fail due to thermal damage. Therefore, the heat dissipation problem of devices and the reliability of equipment have become the key to the development of electronic packaging system technology.

Packaging resin has gradually emerged as the dominant choice for microelectronics packaging materials, owing to its simple production process and low cost. In order to meet the increasing requirements of modern microelectronics packaging, it is necessary to add thermal conductive fillers in packaging resin to improve its overall performance. Notably, metal materials are good heat conductors, and there are electrons that can move freely inside them, so the thermal conductivity of composite materials can be significantly improved. When thermally conductive particles are incorporated into a polymer matrix to form a chain structure or network, the thermally conductive particles act as effective thermal conductors, providing channels for heat transfer and

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ultimately improving the thermal conductivity of the material (Wright et al. 2016). Table 1 lists some studies of metal particles filling polymer matrix materials.

Tekce et al. (2007) studied the thermal conductivity of polyamide composite materials filled with copper powder with different morphologies, and found that the thermal conductivity of composite materials filled with copper powder with different morphologies was similar at low filling rate, but with the increase of filling rate, the thermal conductivity of composite materials filled with fibrous copper powder would increase rapidly. Yaman and Taga (2018) studied the thermal conductivity of unsaturated polyester resin (UPR) matrix composite materials with dendrite copper particles as fillers. The results indicated that the thermal conductivity of the composite materials increases with the increase of copper particle content. When copper particles were added to UPR matrix, a notable outcome emerged that the thermal conductivity of the UPR was up to 21 times higher than that of the pristine UPR. Jasim et al. (2018) prepared the composite material with epoxy (EP) as matrix and aluminum particles as filler by a manual layup method. The results showed that the thermal conductivity of the composite materials filled with 45%Al particles were up to 1.46 W/(m·K), which were about 117% higher than that of the pure epoxy. Chung et al. (2005) discussed the epoxy – aluminum particle composite thermal conductivity from the point of micro structure. As the increase of aluminum particle size, the thermal conductivity of the composite materials would also increase. This was attributed to the reduction of epoxy layer around each particle, resulting in a more stable heat conduction pathway.

Chen and Deng (2019) introduced a novel Zn-Cu hybrid particles and incorporated it into epoxy matrix composites. The results showed that a notable enhancement in thermal conductivity within the EP composites when infused with Zn-Cu particles, surpassing the thermal conductivity of EP composites containing pure Zn powder. This improvement can be attributed to copper's excellent thermal conductivity. Moreover, as the copper content increases, the composite material's thermal conductivity experiences a corresponding rise. The Zn-Cu particles played a pivotal role in shortening the thermal conductivity pathway within the composite materials. Furthermore, they facilitate the mobility of free electrons, thus contributing to an overall improvement in the composite material's thermal conductivity.

Furthermore, nanostructured materials have garnered significant attention owing to their distinctive physical and chemical properties. While silver boasts remarkable thermal conductivity among metals, its high cost necessitates its combination with other fillers or collaborative usage to establish thermal conductivity pathways. This approach helps curtail the quantity of silver used, thus effectively mitigating costs. Hu et al. (2021) incorporated silver nanowires (AgNWs) into EP/S-Al$_2$O$_3$ composites, effectively improving the thermal conductivity and thermal stability of the composite materials. Bai et al. (2020) employed a dip coating process to integrate AgNWs into stereocomplex polylactide fibrous film to further promote the formation of thermal conductivity network. Notably, at a 0.85vol% filling rate of AgNWs, the thermal conductivity achieved an impressive value of 5.95 W/(m·K). Huang et al. (2019) employed silver nanoparticles (AgNPs) to

Table 1 Summary of metal particles filling polymer matrices studies

Metal Fillers	Polymer matrix materials	Remarks
Silver nanoparticles-graphene nanosheets (Chen et al. 2016a)	Epoxy resin	• Ag-GNSs forms an effective thermal conduction network, enhances phonon interface transmission and reduces interface thermal resistance • Volume increases by 400% and the thermal conductivity increases by 300%
Silver flakes, spherical silver particles (Inoue and Liu 2009)	Epoxy resin	• At a mass fraction of 85 wt.%, the thermal conductivity of the silver flake/epoxy resin composite material reaches 5 W/(m·K) • The silver flakes and silver particles are mixed and filled, which can contact in the vertical direction to form better thermal conductivity path, and the thermal conductivity increases
Silver nanoparticles (Rivière et al. 2016) Silver nanoparticles, silver nanowires (Yu et al. 2013)	Poly ether ether ketone (PEEK)	• High aspect ratio fillers can improve thermal conductivity
Copper nanowires (Chen et al. 2016b)	Epoxy resin	• The Cu mass fraction is 0.12 wt.%, and the thermal conductivity of the composite material is 2.59 W/(m·K)
Silver powder treated with iodination (Wu et al. 2014)	Epoxy resin	• The thermal conductivity of the composite material is 13.5 W/(m·K)
FeCr/Al2O3 composite particles (Kim et al. 2014)	Polyvinyl Chloride (PVC)	• The composite particle interface has excellent thermal contact conductivity

Fig. 1 The morphology of copper powder particles
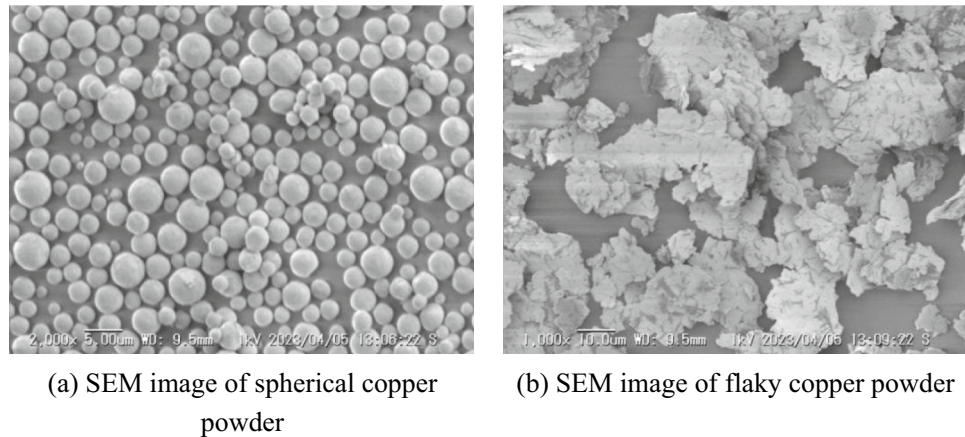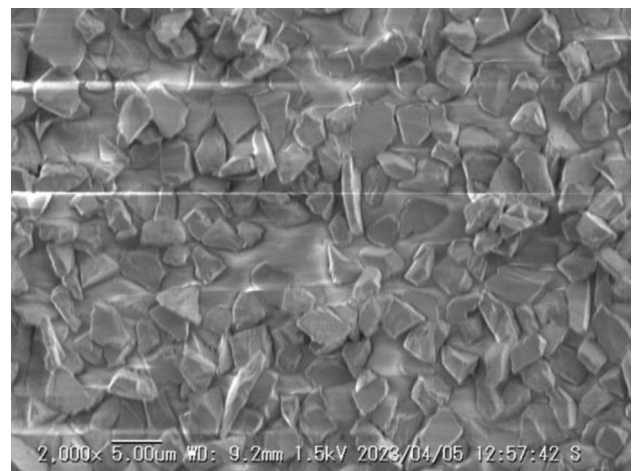

(a) SEM image of spherical copper powder

(b) SEM image of flaky copper powder

significantly facilitate the construction of a thermal conductivity framework involving reduced graphene oxide (rGO), leading to a marked enhancement in the thermal conductivity of polystyrene (PS). Correspondingly, Chen et al. (2019) applied a strategy of AgNP loading onto boron nitride nanosheets, effectively instigating the development of thermal conductivity networks and thereby amplifying the thermal conductivity of epoxy matrix composites.. Additionally, copper, due to its high thermal conductivity and abundant availability, has garnered considerable interest, particularly in the context of copper nanowires. Ahn et al. (2015) prepared copper nanowire/epoxy composites, improving their thermal properties by applying a TiO_2 coating to the copper nanowires. Similarly, Chen et al. (2016b) prepared a novel composite material by incorporating single crystal copper nanowires as fillers into an epoxy matrix. Remarkably, the introduction of 0.12 vol% copper nanowires resulted in an impressive thermal conductivity of 2.59 W/(m·K).

With the escalating power density of electronic devices, microelectronic packaging requires composite materials with higher thermal conductivity. However, due to the resistance between the base material and the filler, the heat transfer performance of the composite materials is greatly limited. Liu et al. (2017) devised a hybrid reduced graphene oxide encapsulated copper sphere (Cu@rGO) as filler, epoxy as matrix of composite material. The results showed that the presence of rGO can enhance the oxidation resistance of copper and reduce the interface thermal resistance between copper and epoxy. Consequently, this synergy elevates the composite's thermal conductivity. Particularly noteworthy is the composite laden with 80 wt% Cu@rGO, achieving a thermal conductivity value of 7 W/(m·K). Mao et al. (2019) studied the thermal conductivity of epoxy composite materials infused with core–shell structured $Al@Al_2O_3$ fillers, revealing a linear correlation between filler content and composite material thermal conductivity increase. Zhou et al. (2012) fabricated a core–shell composite with $Ag@SiO_2$ nanoparticles as the filler and polyimide (PI) as the matrix, and

compared it with the core–shell nanocomposites with self-passivated aluminum nanoparticles. The results indicated that the core–shell $Ag@SiO_2$ nanoparticles could significantly improve the thermal conductivity of the composite materials, with a highest thermal conductivity of 7.88 W/(m·K).

Copper has excellent electrical and thermal conductivity, with a thermal conductivity of 389 W/(m·K), so it is frequently employed in the preparation of polymer materials with good thermal conductivity and low insulation requirements. Nevertheless, the chemical properties of copper are active, and its powder succumbs to oxidation when exposed to air, subsequently resulting in the formation of copper oxide and cuprous oxide films on its surface, reducing its thermal conductivity. Consequently, it is necessary to solve the problem that copper powder is easily oxidized in the preparation process. Additionally, the diamond primarily consists of carbon, which the four isolated electrons of carbon atoms are involved in bonding to form C–C bonds, so diamond has strong hardness, high melting point, good insulation and other characteristics, in addition, it has good thermal conductivity.

Fig. 2 Morphology diagram of diamond particles

Table 2 Basic properties of copper powder particles

	Average size μm	Thermal conductivity W•(m·K)$^{-1}$	Density g·cm^{-3}	Specific heat J·(kg·℃)$^{-1}$
Spherical copper powder	5	389	8.9	390
Flaky copper powder	10			

In this study, copper powder and diamond particles were used as filler, epoxy as matrix. The composite materials are synthesized using a vacuum-assisted mechanical stirring technique. The investigation revolves around assessing the thermal expansion coefficients of diverse composites using the laser flash method, subsequently allowing the calculation of their thermal conductivity coefficients. The effects of copper powder filling rate, copper powder morphology, diamond filling rate, and thermal conductivity of particles on the thermal conductivity of composites were studied.

Experiment Preparation

Experimental Material

The copper powder used in this experiment was provided by Xuzhou Jie Innovative Material Technology Co., Ltd. The SEM images of its morphology are shown in Fig. 1. Diamond particles were provided by Henan Zhongyuan Diamond Tools Co., Ltd. The SEM images of their morphology are shown in Fig. 2.

As can be seen from Fig. 1, spherical copper powder particles have good sphericity and uneven particle size. The particle size of spherical copper powder is mainly distributed between 3 ~ 5 μm. The size of flake copper powder is about 10 μm, and the maximum size is 30 μm. The parameters of copper powder are shown in Table 2.

As can be seen from Fig. 2, diamond particles are irregular polyhedra with a particle size of about 5 μm. The parameters of diamond particles are shown in Table 3.

Table 3 Basic properties of diamond particles

|	Average size μm	Thermal conductivity W•(m·K)$^{-1}$	Density g·cm^{-3}	Specific heat J·(kg·℃)$^{-1}$
Diamond particles	5	200 ~ 2000	3.5	450

Experimental Methods

The preparation method of the composite thermal conductive material is obtained through repeated exploration. The experimental process is illustrated in Fig. 3. The specific methodologies are detailed below:

1. The thermal conductive copper powder and oxalic acid were put into the beaker and dispersed in the ultrasonic cleaning instrument to remove the oxide layer on the surface of the copper powder.
2. Filter and collect the copper powder, clean the residual oxalic acid on the surface of the copper powder with anhydrous ethanol, and dry it in a vacuum drying oven.
3. Put the diamond particles and anhydrous ethanol into the beaker, disperse them in the ultrasonic cleaning instrument, wash the oil and other impurities on the surface of the particles, filter and dry the diamond particles.
4. Take a certain quality of epoxy in the beaker as the base material, prepare 20 parts of curing agent for every 100 parts of epoxy.
5. Put thermal conductive copper powder and diamond particles with different mass fractions into beakers respectively. The rate of copper powder with different mass fractions is shown in Tables 4 and 5, and the rate of diamond is shown in Table 6.
6. Put the mixture into a vacuum container, stir it for 40 min under the conditions of absolute pressure less than 5 kPa and stable temperature at 40 °C to remove a large number of bubbles in the mixture.
7. Put the beaker into the ultrasonic cleaning instrument and take it out after 20 min of ultrasound to remove the remaining tiny bubbles in the mixture.
8. Pour the curing agent into the mixture, stir it in a vacuum container for 10 min, take out and pour into a PTFE mold sprayed with release agent on the surface, and cure at room temperature for 12 h.

Fig. 3 Preparation process of composite materials
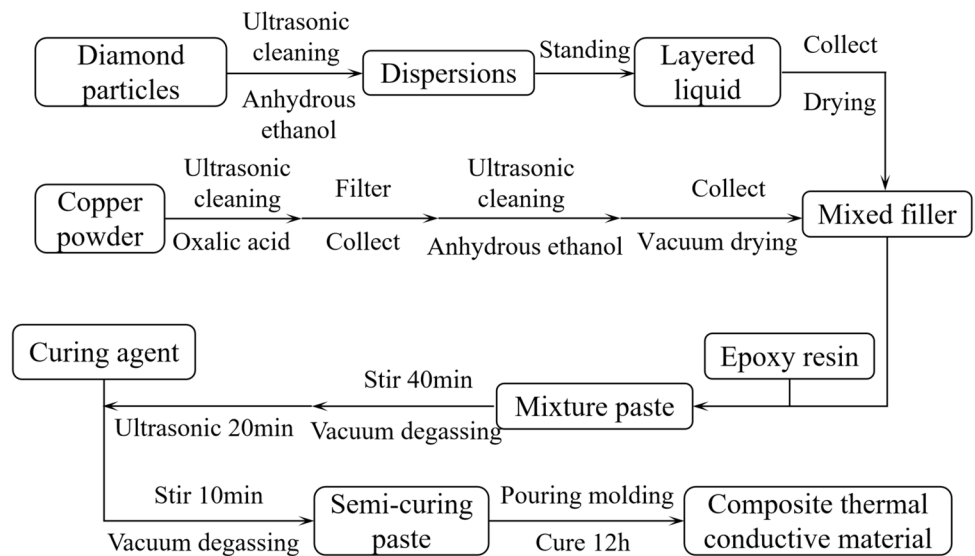
Table 4 Material dosage under different mass fraction of 30 μm flaky copper powder

Volume filling rate (vol.%)	Mass filling rate (wt.%)	Flake copper powder (g)	Epoxy dosage (g)	Curing agent dosage (g)
4.6	30	2.6	5.0	1.0
7.0	40	4.0	5.0	1.0
10.1	50	6.0	5.0	1.0

Experimental Results

Effect of Spherical Copper Powder Filling Rate on the Composite Thermal Conductivity Materials

The composite thermal conductive material was prepared by casting molding process. This involved employing epoxy as the matrix materi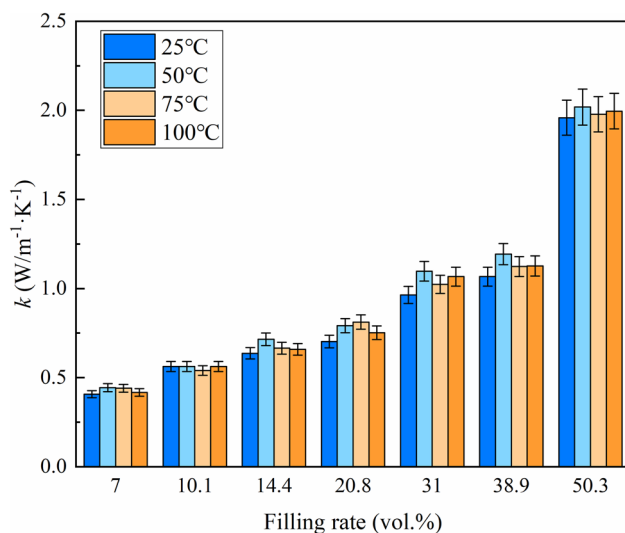al in a mass ratio of 100 parts, along with a curing agent in a mass ratio of 20 parts. The filler constituents comprised 5 μm spherical copper powder in quantities of 80 parts, 120 parts, 180 parts, 280 parts, 480 parts, 680 parts, and 1080 parts. These quantities correspond to volume fractions of 7.0 vol.%, 10.1 vol.%, 14.4 vol.%, 20.8 vol.%, 31.0 vol.%, 38.9 vol.%, and 50.3 vol.%, respectively. When the filler concentration is lower, the saturation of the mixture will be lower and its contact with the binder resin will be better, but at this time the fillers are enveloped by the mixture resin, which is difficult to establish a thermal path between the fillers, so the thermal conductivity decreases. On the contrary, if too much filler material is added, although the thermal conductivity of the mixture will be increased, the resin particles will be difficult to be wetted, so the resulting composite structure will be easily pulverized. Therefore, the maximum filler concentration is 50.3 vol% in this study. The relationship between the filling rare of spherical copper powder and the thermal conductivity of the composite materials at different temperatures is depicted in Fig. 4.

Table 5 Material dosage with different mass fraction of 5 μm spherical copper powder

Volume filling rate (vol.%)	Mass filling rate (wt.%)	Flake copper powder (g)	Epoxy dosage (g)	Curing agent dosage (g)
7.0	40	4.0	5.0	1.0
10.1	50	6.0	5.0	1.0
14.4	60	9.0	5.0	1.0
20.8	70	14.0	5.0	1.0
31.0	80	24.0	5.0	1.0
38.9	85	34.0	5.0	1.0
50.3	90	54.0	5.0	1.0

Table 6 Material dosage under different mass fraction of diamond particles

Volume filling rate (vol.%)	Mass filling rate (wt.%)	Flake copper powder (g)	Epoxy dosage (g)	Curing agent dosage (g)
3.1	10	0.7	5.0	1.0
6.7	20	1.5	5.0	1.0
10.9	30	2.6	5.0	1.0
16.0	40	4.0	5.0	1.0
22.2	50	6.0	5.0	1.0
30.0	60	9.0	5.0	1.0
40.0	70	14.0	5.0	1.0

Fig. 4 Effect of spherical copper powder filling rate on thermal conductivity of composites at different temperatures
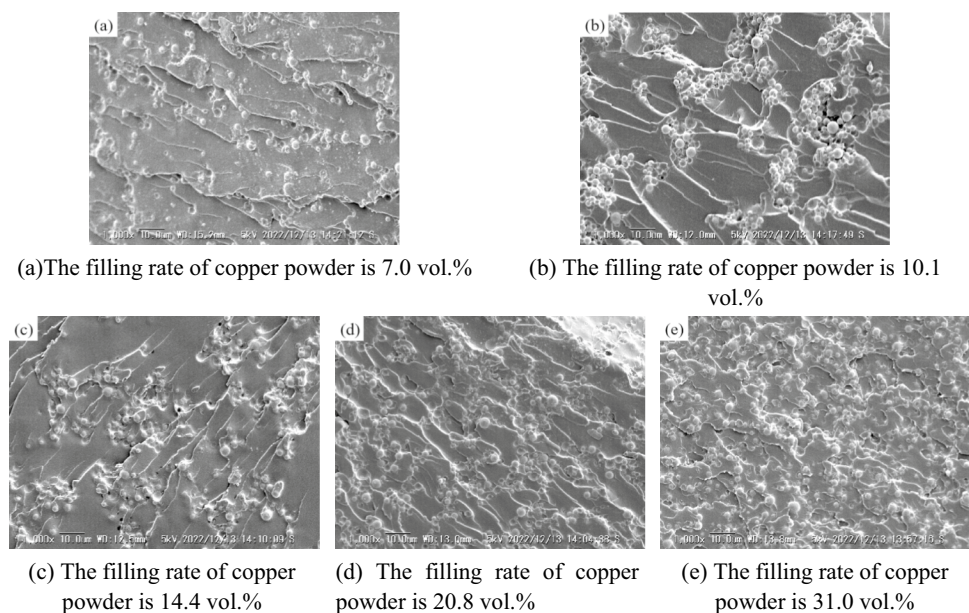
As can be seen from Fig. 4, it is evident that, under the same filling rate, the thermal conductivity of the composite material exhibits minimal fluctuations with the increase of temperature, indicating that the influence of temperature on the thermal conductivity of the composite material is relatively unconspicuous. Conversely, increasing the copper powder filling rate can effectively improve the thermal conductivity of the composite material. Specifically, the thermal conductivity of the composite increases with the increase of copper powder filling. When the volume filling rate is 50.3 vol.%, the thermal conductivity reaches a peak value of 2.01 W/(m·K). It is worth noting that when the copper powder
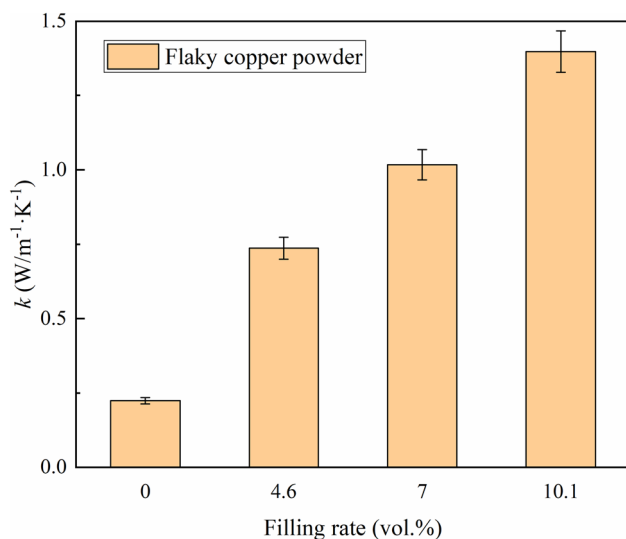
filling rate remains below 30 vol.%, the thermal conductivity of the composite materials increases slowly. While exceeding the 30 vol.% filling rate leads to a more rapid increase in the thermal conductivity of the composite materials.

Figure 5 depicts the SEM image of the cross section of the composite material under different filling rate of 5 μm spherical copper powder. Notably, when the filling rate of the spherical copper powder is lower than 10 vol.%, the interior structure of the composite material displays an "island" shape, as shown in Fig. 5(a) and (b). The spherical copper powder exhibits a uniform dispersion within the epoxy matrix. At extremely low filler concentrations, copper particles with high thermal conductivity are enveloped by the matrix resin, preventing them from making contact with each other. Consequently, thermal conductivity has a slight improvement at low concentrations. Specifically, at a 7.0 vol.% filling rate, the thermal conductivity reaches 0.45 W/(m·K). At a 10.1 vol.% filling rate, the thermal conductivity escalates to 0.56 W/(m·K).

When the filling rate of copper powder increases from 10 vol.% to 20 vol.%, the internal structure of the composite material undergoes a transition from "island" to "chain" shape. This evolution is evident in Fig. 5(c) and (d), which respectively illustrate the cross-sectional morphology of the composite material at 14.4 vol.% and 20.8 vol.% filling ratios. With the increase of the filling rate, the spherical copper powder particles inside the composite aggregate a large number of short chains with each other. It's important to note that the copper powder particles transmit heat through free electrons. Consequently, at the interface between the copper powder particles and the matrix, electron–phonon scattering occurs, disrupting the establishment of an efficient thermal conductivity pathway. As a result, the rise in the composite

Fig. 5 SEM morphology of 5 μm spherical copper powder composite sections at different filling rates

(a)The filling rate of copper powder is 7.0 vol.%

(b) The filling rate of copper powder is 10.1 vol.%

(c) The filling rate of copper powder is 14.4 vol.%

(d) The filling rate of copper powder is 20.8 vol.%

(e) The filling rate of copper powder is 31.0 vol.%

Fig. 6 Effect of filling ratio of flaky copper powder on thermal conductivity of composite materials at room temperature

material's thermal conductivity is relatively gradual. Specifically, at a filling rate of 14.4 vol.%, the thermal conductivity attains 0.65 W/(m·K), while at a filling rate of 20.8 vol.%, it further escalates to 0.79 W/(m·K).

Upon reaching a copper powder filling rate reaches 30 vol.%, the internal structure of the composite material changes from "chain" to "network" shape. This transformation is visibly demonstrated in Fig. 5(e) and (f), which illustrate the cross-sectional morphology of the composite material at filling rate of 31 vol.% and 38.9 vol.%. At this stage, the copper powder particles establish direct contact with one another, and the previously formed short chains within the composite begin to intertwine, forming continuous thermal conduction paths. This structural evolution significantly enhances the composite material's thermal conductivity. Notably, at a filling rate of 38.9 vol.%, the thermal conductivity reaches 1.2 W/(m·K).

As the copper powder filling rate rises to 50 vol.%, the contact region between copper powder particles expands, as shown in Fig. 5(g). The heat conduction path emerges between the particles via electron–electron coupling. This formation of

a heat conduction pathway allows the optimal transfer of heat, consequently reducing the interface's energy consumption and promoting efficient heat conduction along this optimized pathway. Remarkably, when the filling rate attains 50.3 vol.%, the thermal conductivity reaches 2.01 W/(m·K), marking a significant 874% increase relative to the matrix material.
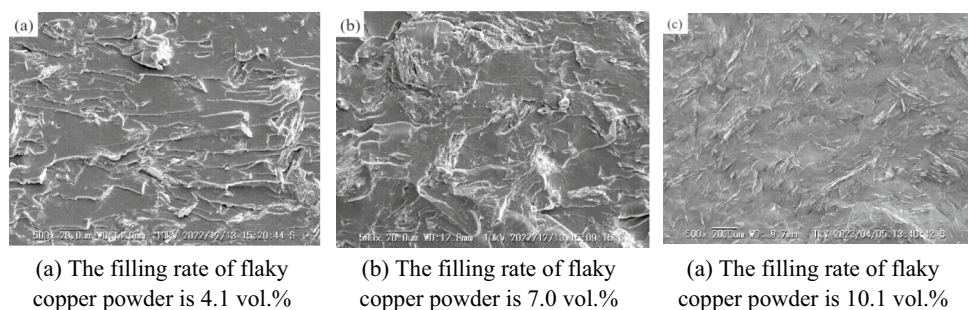
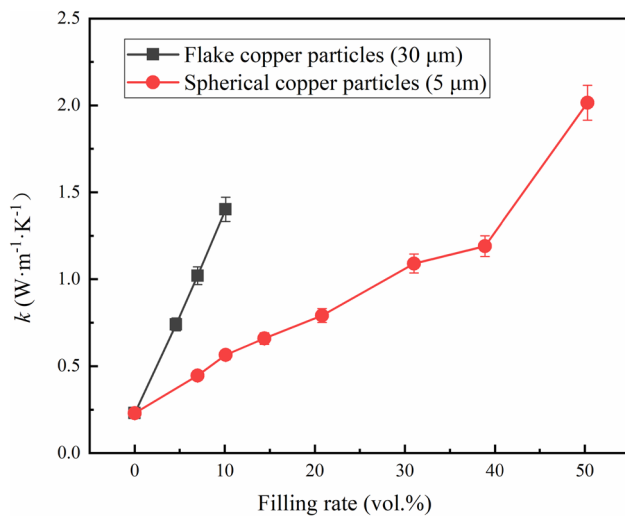## Effect of Flaky Copper Powder Filling Rate on Thermal Conductivity of Composite Materials

The composite thermal conductive materials were prepared by casting molding process utilizing epoxy as matrix, comprising 100 parts mass and a curing agent with a mass of 20 parts. Additionally, 30 μm flake copper powder was incorporated as filler, with qualities of 52 parts, 80 parts and 120 parts, corresponding to volume fractions of 4.6 vol.%, 7.0 vol.% and 10.1 vol.%, respectively. The relationship between the filling of flake copper powder and the thermal conductivity of the composite materials at room temperature is shown in Fig. 6. Evidently, the inclusion of flake copper powder contributes significantly to the enhancement of the composite's thermal conductivity. At a filling rate of 10.1 vol.%, the thermal conductivity reaches 1.4 W/(m·K).

Figure 7 presents the SEM image of the cross section of the composite materials under different filling rate of flake copper powder. As a two-dimensional thermal conductivity material, flake copper powder can be interconnected to form short chains at a low filling rate, as shown in Fig. 7(a). The inner direction of the copper powder surface efficiently conducts heat, consequently inducing a rapid increase in the composite material's thermal conductivity. Notably, at a filling rate of 4.6 vol.%, the thermal conductivity attains 0.74 W/(m·K). With the increase of the filling rate of flake copper powder, the short chains are connected to each other to form more thermal conductivity networks. As shown in Fig. 7(b) and (c), when the filling rate of flake copper powder is only 7.0 vol.%, the thermal conductivity is 1.02 W/(m·K). When the filling rate of flake copper powder reaches 10.1 vol.%, the thermal conductivity is 1.4 W/(m·K), marking a 609% enhancement relative to the matrix material.

Figure 8 displays the effect of different copper powder sizes on the thermal conductivity of the composite materials

Fig. 7 SEM morphology of composite section under different filling rates of flaky copper powder
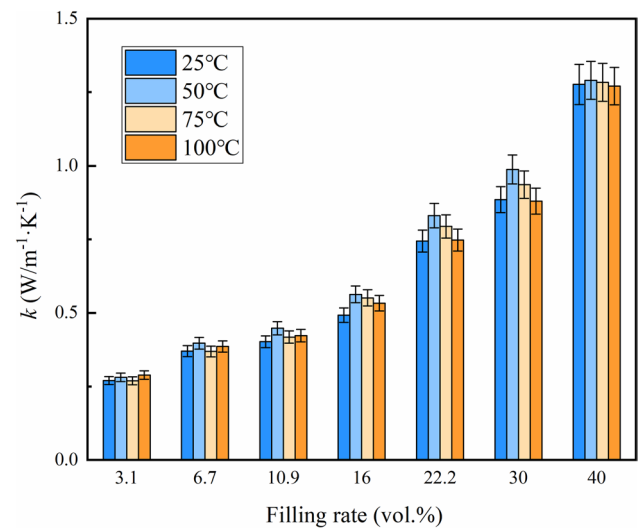

(a) The filling rate of flaky copper powder is 4.1 vol.%

(b) The filling rate of flaky copper powder is 7.0 vol.%

(a) The filling rate of flaky copper powder is 10.1 vol.%

Fig. 8 Effect of copper powder with different sizes on thermal conductivity of composites at room temperature

Fig. 9 Effect of diamond particle filling rate on thermal conductivity of composites at different temperatures

at room temperature. At a constant filling rate, filling thermal conductive particles with larger size can better enhance the thermal conductivity of the composite material. This phenomenon arises due to the smaller contact area between larger particles and the matrix, resulting in reduced energy loss at the interface and heightened thermal conductivity efficiency. Compared with zero-dimensional spherical particles, two-dimensional flake thermal conductive particles are more easily connected to form short chains, thus effectively improving the thermal conductivity of composite materials at a lower filling rate. However, substantial filling of flake thermal conductive particles can prompt particle aggregation and hinder matrix wettability, limiting surface infiltration. Consequently, the increase of the gaps in the composite materials affect the enhancement of thermal conductivity.

Effect of Diamond Filling Rate on Thermal Conductivity of Composite Materials

The composite thermal conductive materials were prepared by casting molding process, utilizing epoxy as the matrix with a mass of 100 parts and a curing agent with a mass of 20 parts. Diamond particles were incorporated as fillers in quantities of 14 parts, 30 parts, 52 parts, 80 parts, 120 parts, 180 parts, and 280 parts. These quantities correspond to volume fractions of 3.1 vol.%, 6.7 vol.%, 10.9 vol.%, 16.0 vol.%, 22.2 vol.%, 30.0 vol.%, and 40.0 vol.% respectively. The relationship between the filling rate of diamond particles and the thermal conductivity of composite materials at different temperatures is shown in Fig. 9.

At the same filling rate, the composite material's thermal conductivity exhibits minimal fluctuations with temperature shif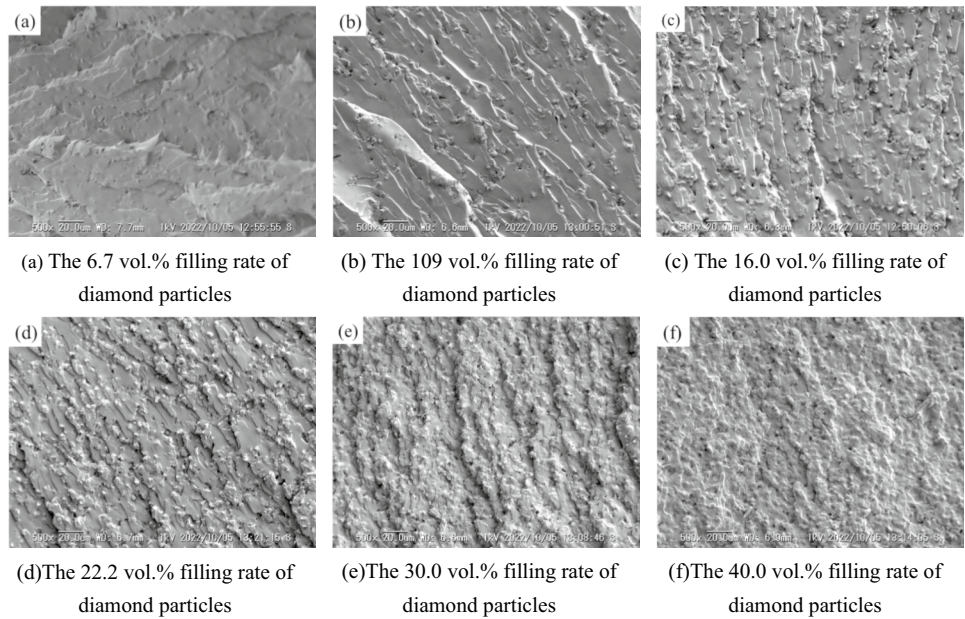ts, indicating that the influence of temperature on the thermal conductivity of the composite material is not obvious. It can be seen from the Fig. 9 that filling diamond particles can effectively improve the thermal conductivity of the composite materials. With the increase of diamond particle filling rate, the thermal conductivity of the composite materials increases gradually. When the volume filling rate is 40.0 vol.%, the thermal conductivity is 1.23 W/(m·K). When the diamond particle filling rate is lower than 16.0 vol.%, the thermal conductivity of the composite increases slowly. However, exceeding the 16 vol.% filling rate triggers a more rapid increase in the composite's thermal conductivity.

Figure 10 shows the SEM image of the cross section of the composite materials under different filling rate of diamond particles. When the filling rate of diamond particles is lower than 10 vol.%, the interior structure of the composite materials has an "island" shape, as depicted in Fig. 10(a). The uniform dispersion of diamond particles within the epoxy matrix is obvious. Due to the low filling rate, the diamond particles remain physically detached from the epoxy, contributing to a slight increase in the composite material's thermal conductivity. Specifically, at a 6.7 vol.% filling rate, the thermal conductivity is 0.38 W/(m·K).

As the diamond particle filling ratio escalates from 10 vol.% to 30 vol.%, the internal structure of the composite materials undergoes a transition from "island" to "chain" shape. This transformation is exemplified in Fig. 10(b)~(d), portraying the cross-sectional morphologies of the composites at filling rates of 10.9 vol.%, 16 vol.%, and 22.2 vol.% respectively with the increase of the filling rate, the diamond particles within the composite bonded to each other to form a large number of short chains. However, the thermal conductivity path is different to be established, resulting in a slowly increase of the thermal conductivity of the composite

Fig. 10 SEM morphology of composite section under different diamond particle filling rates


(a) The 6.7 vol.% filling rate of diamond particles

(b) The 109 vol.% filling rate of diamond particles

(c) The 16.0 vol.% filling rate of diamond particles

(d)The 22.2 vol.% filling rate of diamond particles

(e)The 30.0 vol.% filling rate of diamond particles

(f)The 40.0 vol.% filling rate of diamond particles

materials. Specifically, at a 10.9 vol.% filling rate, the thermal conductivity attains 0.42 W/(m·K). This value increases to 0.55 W/(m·K) at a 16.0 vol.% filling rate, and further rises to 0.84 W/(m·K) at a 22.2 vol.% filling rate.

When the diamond particle filling rate reaches 30.0 vol.%, the internal structure of the composite materials transitions from "chain" to "network" shape. Figure 10(e)~(f) elucidate the cross-sectional morphology of the composite material at filling ratios of 30.0 vol.% and 40.0 vol.%. This evolution triggers the interlinking of short chains within the composite, culminating in the establishment of a continuous thermal conduction pathway. The diamond particles contact each other, leading to a reduction in the contact area between particles and the matrix. This results in minimized energy dissipation at the interface, enabling efficient heat conduction along the optimal thermal conductivity pathway and significantly enhancing the composite material's thermal conductivity. Remarkably, at a 30.0 vol.% filling rate, the thermal conductivity achieves 0.98 W/(m·K). Upon reaching a 40.0 vol.% filling rate, the thermal conductivity further escalates to 1.23 W/(m·K), representing a substantial 535% enhancement relative to the matrix material.

Effect of Thermal Conductivity of Particles on Thermal Conductivity of Composites

It can be seen from the Fig. 11 that at the same filling rate, when the particles with high thermal conductivity are filled, the thermal conductivity of the composite materials increases rapidly. Illustratively, at a 30 vol.% filling rate, the thermal conductivity of the composite materials filled with 5 µm spherical copper powder and diamond particles reached

1.05 W/(m·K) and 0.96 W/(m·K), respectively. Copper particles inherently rely on electrons for heat conduction, which endows them with superior thermal conductivity compared to alumina particles that rely on phonons for heat conduction. In composite materials, as heat transfer through the interface between particles and the matrix, the lattice vibration of matrix materials affects the movement of free electrons within metal particles, resulting in electron–phonon interaction, which limits the rapid heat conduction of across the interface. Consequently, the potential for significantly enhancing the thermal conductivity of composite materials through
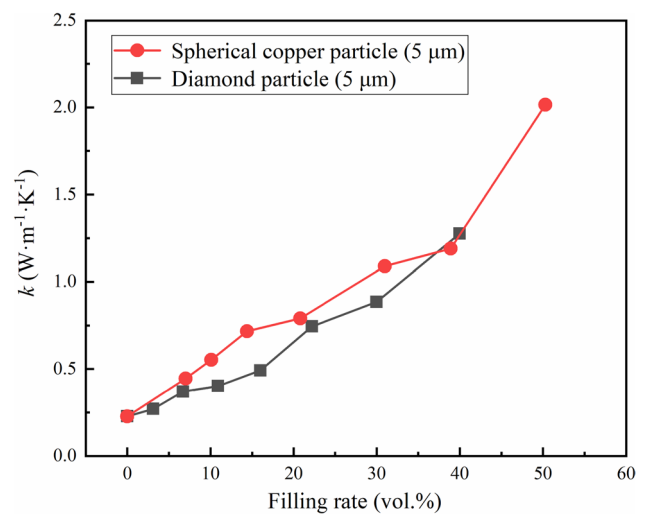
Fig. 11 Effect of the filling rate on the thermal conductivity of the composite materials with different thermal conductivity at room temperature

the introduction of high thermal conductivity particles is constrained. Simultaneously, in contrast to spherical particles, irregular polyhedral diamond particles encounter limitations when employed at elevated filling rates. Despite the expansion of the contact area between particles, epoxy matrix wettability constraints result in incomplete void filling. In turn, voids generated within the composite material also impede further advancements in thermal conductivity enhancement.

Conclusion

In this study, copper powder and diamond particles are used as filler, with epoxy serving as the matrix. The fabrication of composite materials was realized via a vacuum-assisted mechanical stirring technique. The thermal expansion coefficient of various composite materials was measured by laser flash method, followed by subsequent thermal conductivity calculations. The effects of copper powder filling rate, copper powder morphology, diamond filling rate, and thermal conductivity of particles on the thermal conductivity of composite materials were studied. The conclusions are as follows:

1. The thermal conductivity of the composite materials increases with the filling rate of copper powder. Notably, at a 50.3 vol.% filling ratio of 5 μm copper powder, the thermal conductivity achieves 2.01 W/(m·K), marking an impressive 874% surge relative to the matrix. Similarly, for 5 μm diamond particles, a 40.0 vol.% filling ratio corresponds to a thermal conductivity of 1.23 W/(m·K), signifying a substantial 535% enhancement compared to the matrix.

2. At the same filling rate, the thermal conductivity of the composite materials can be better improved by filling the thermal conductivity particles with larger particle size. Compared with zero-dimensional thermal conductive particles, two-dimensional thermal conductive particles prove more effective in enhancing composite material's thermal conductivity at lower filling rates. Nevertheless, when the flake thermal conductive particles are filled with a high proportion, particle aggregation is easy to occur, and the wettability of the matrix is limited.

3. The thermal conductivity of composites increases approximately linearly with the amount of filling and the thermal conductivity of fill particles themselves. After a certain threshold value at higher concentrations, the filled particles are prone to aggregation over a large area, which will be difficult to be wetted by epoxy resin. Even there is a higher thermal conductivity, the resulting composites will be easily pulverized.

Declarations

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